



Superheating, Supercooling, and Hysteresis in Semiconductor Nanocrystals

MSD researchers led by Daryl Chrzan, Joel Ager, and Eugene Haller, making use of the microscopes at the National Center for Electron Microscopy, have discovered that nanocrystals of germanium (Ge) embedded in silica glass remain solid to nearly 200 K above the melting temperature of germanium in bulk. Equally surprising, the melted nanocrystals remain molten to 200 K below the bulk melting point before they resolidify. Such a large and nearly symmetrical “hysteresis”—the divergence of melting and freezing temperatures above and below the bulk melting point—had never before been observed for embedded nanoparticles and illustrates the type of new and surprising physical phenomena which can be observed at the nanoscale.

For almost a hundred years, theorists and experimenters have studied how the size of a crystal affects the transition between melting and freezing. For most crystalline materials, the smaller the crystal the lower the melting temperature: the melting temperature of a free-standing nanocrystal may be more than 300 K below the melting temperature of the same material in bulk. Classical thermodynamic analysis explains this phenomenon well. For most materials, interface energies between solid and vapor favor the formation of a liquid surface layer as the temperature increases and this layer continues to grow until the entire object is melted. The melting point change results from the fact that this liquid layer forms more readily at lower temperatures as the proportion of surface to volume increases.

However, for embedded nanocrystals, the interface energies will be different from those for free-standing nanocrystals and this could lead to different behavior. To explore this experimentally, 5 nm diameter germanium (Ge) particles in an amorphous matrix of silica glass were studied. Melting and freezing measurements were performed *in situ* in a transmission electron microscope at Berkeley Lab’s National Center for Electron Microscopy using a high temperature stage. By directing the electron beam through a thinned sample, diffraction rings produced by the crystal lattices of the embedded particles were observed. When the particles began to melt, the diffraction rings weakened and finally vanished, allowing precise measurement of the temperature at which the embedded particles melted. As the temperature was lowered again, the reappearance of the diffraction rings signaled resolidification. For repeated heating/cooling cycles, the particles melted about 200 K higher than bulk (superheating) and resolidified 200 K lower than bulk (supercooling).

Superheating had been observed before for nanocrystals in crystalline matrices—lead in aluminum is a well-studied case. In this system, the similar lattice structures of the two crystals can “lock up,” suppressing the vibration of the nanoparticles’ surface atoms that would lead to melting. However, in the present case of nanocrystals in an amorphous matrix, this mechanism cannot occur. To explain the Ge/silica results, the traditional theory of nucleation developed in the 1950’s for free-standing particles required modification to take into account the nanocrystal/matrix interface. Using the known surface energies for Ge liquid, solid, and vapor in contact with silica, *depression* of the equilibrium melting point for Ge nanocrystals was predicted, which is the opposite of what was observed. However, consideration of the kinetic path to melting resolved the puzzle. As the nanoparticle heats up, a liquid nucleus must achieve a critical size before it can spread and entirely melt the nanocrystal. The total energy of this nucleated melt is a function of, among other factors, the surface energies of the germanium (liquid)—silica; germanium (liquid)—germanium (solid); and germanium (solid)—silica (solid) interfaces, which vary with respect to each other with the size of the germanium embedded. With germanium nanoparticles, the total surface energy creates a kinetic barrier sufficiently large to prevent melting on experimentally accessible time scales (hours) until the temperature reaches 200 K above bulk melting point. The balance among interface energies involved in the transition from solid to liquid at the melting temperature creates a similar roadblock in the opposite direction: an energy barrier to freezing.

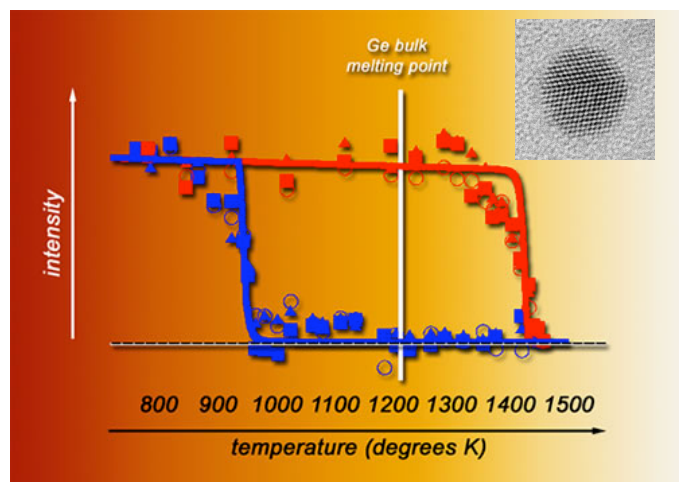
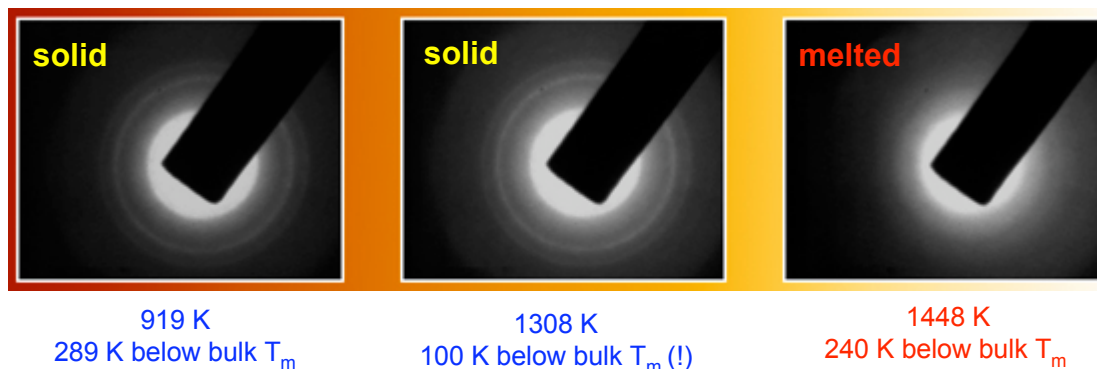
The results illustrate the novel types of behavior that can be created in nanoscale systems. The researchers are now considering other embedded nanocrystals which can display melting/freezing hysteresis, with an eye towards their use in data storage and other applications.

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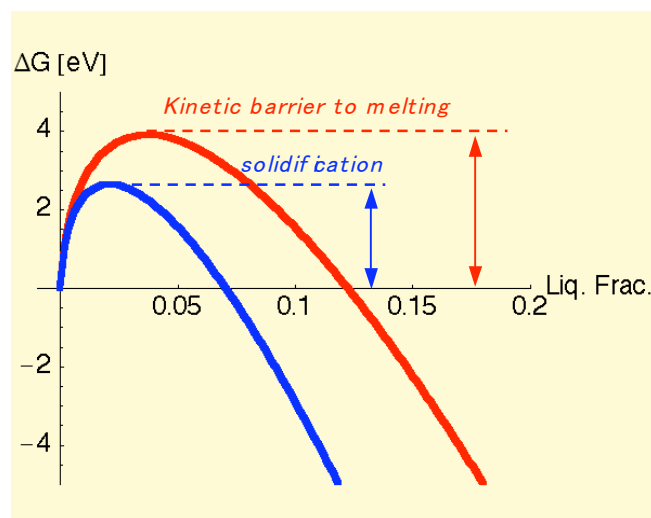
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The unexpectedly high melting point of germanium nanocrystals embedded in silica glass was measured inside a transmission electron microscope (right). Electron diffraction patterns (bright rings) from the crystalline lattice structure—indicative of the solid state—persist until the crystal melts, at a temperature more than 230 K above the melting point of bulk germanium (~1211 K).



Melting (red), at 1448 K, and cooling (blue), at 950 K, are shown in the plot of intensity of electron diffraction rings against temperature (above). A nearly symmetrical hysteresis loop about the bulk melting temperature of 1211 K is seen. Solid lines represent the prediction of the new LBNL theory developed to explain this phenomenon. (Insert is typical 5 nm Ge nanocrystal used in these studies.)



A new LBNL theory to explain this unusual melting/resolidification phenomenon is based on the fact that melting requires the formation of a critical nucleus of molten material and solidification similarly requires a critical nucleus of solid material to proceed. There is an energy barrier to this critical nucleus formation in both directions (red, melting; blue, solidification) resulting in the observed hysteresis.